Full Anisotropy of the Stark Effect on the 1B2u ← 1Ag Electronic Transitions of Tetracene and Pentacene in a p-Terphenyl Host Crystal

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FULL ANISOTROPY OF THE STARK EFFECT ON THE $^1B_{2u} \leftarrow {}^1A_g$ ELECTRONIC TRANSITIONS OF TETRACENE AND PENTACENE IN A *p*-TERPHENYL HOST CRYSTAL

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The results of a low temperature Stark-effect study on the visible short axis polarized singlet transitions of tetracene and pentacene are presented and discussed.

The full anisotropy of the Stark effect could be obtained reliably only by using bipolar electric field modulation together with an optical multichannel detection system. This system is also briefly described in this paper.

Using the anisotropic Lorentz approximation the difference polarizability tensor components are found to be: for tetracene $\Delta\alpha_{LL} = 29 \pm 3$ Å^3, $\Delta\alpha_{MM} = 25 \pm 4$ Å^3, $\Delta\alpha_{NN} = 5 \pm 5$ Å^3; and for pentacene $\Delta\alpha_{LL} = 53 \pm 4$ Å^3, $\Delta\alpha_{MM} = 90 \pm 8$ Å^3, and $\Delta\alpha_{NN} = -11 \pm 9$ Å^3. The paper emphasizes that these numbers, due to the inherent approximations of the Lorentz approximation, should be handled with great caution.

1. Introduction

In a previous paper [1], we reported the first results of a high resolution second order Stark effect study on the electronic origins of the $^1B_{2u} \leftarrow {}^1A_g$ absorption system of tetracene and pentacene in a *p*-terphenyl host crystal at 1.8 K. The main conclusion of that paper was that, in principle, from such single crystal studies the full anisotropy of the *difference* polarizability tensor can be obtained, which is not possible from measurements in solutions [2] or solid films [3]. We felt it desirable to show that indeed this can be done, and the present paper contains the results of a Stark effect study along three orthogonal directions. From further experimentation on the *p*-terphenyl mixed crystal system it became clear that the tin oxide coated pyrex electrodes in combination with unipolar electric field modulation were not a favourable choice for a Stark effect study on this system. This was most evident in the observed large decrease in time of the measured electric field induced shifts, and the bad reproducibility of the results obtained. We must conclude, therefore, that the previously reported values [1] of the long axis difference polarizability of tetracene and pentacene are far too low. Most of these effects were overcome by changing to stainless steel electrodes [4] and bipolar electric field modulation.

Because our original Stark set-up appeared to be not sensitive enough to detect the small shifts that were induced along the *a*-axis of the *p*-terphenyl crystal, an optical multichannel analyzing system was developed. This system greatly improved the signal to noise ratio and accuracy of the Stark effect measurements.

However, firm as our *experimental* results are now, it has recently [5–7] become increasingly clear that, in a crystal as *p*-terphenyl, there is no unique way of analyzing the measured Stark shifts in terms of molecular parameters. In this paper we therefore emphasize the experimentally obtained results and realize that the polarizability changes obtained with the anisotropic Lorentz approximation must be viewed with great suspicion.

2. Experimental

The *p*-terphenyl, used as the host crystal, was purified by repeated zone refining. Single crystals, doped simultaneously with tetracene and pentacene were grown in a temperature controlled Bridgman furnace. *p*-Terphenyl crystals are monoclinic ($P2_1/a$) [8] at room temperature, with two molecules in the unit cell. The quality and orientation of the crystals was checked with

a polarizing microscope. Crystals of about 1 mm thickness, cleaved or cut in the desired direction, were mounted between polished stainless steel electrodes, while small springs were used to ensure contact between the crystal and the electrodes. Occasionaly tin oxide coated pyrex electrodes were used, but all polarizability changes reported here were obtained using stainless steel electrodes.

The optical measurements were performed using a 1 meter 1704 Spex provided with a 300 grooves/mm echelle grating (Bausch and Lomb) used in 10th or 11th order. The resolution was about 0.5 cm^{-1} under the experimental conditions. A 1000 watt Xenon lamp was used as a light source while a Spex 'Minimate' served as predisperser to prevent photochemical effects in the crystal and overlap of different orders in the spectrometer.

An RCA 4532 A silicon diode array camera tube mounted in a CTC-6000 camera (ITC) was used as a multichannel analyzer. It was mounted on the spectrometer, in such a way, that each line of the TV camera contained information about a specific wavelength region. The signal of each line was fed into a corresponding channel of a computer of average transients (CAT, Varian C-1024, modified to allow count up and count down of the incoming signal). By square wave modulation of the high voltage applied over the crystal and simultaneously switching of the count up/count down action of the CAT, a modulation spectrum was obtained. This was stored in 512 of the CAT's channels, corresponding to a spectral width of 44 cm^{-1} in 10th order at 17000 cm^{-1}. The absorption spectrum was stored in the remaining 512 channels of the CAT.

The block diagram in fig. 1 shows major elements of the system, which is described in more detail elsewhere [9]. Also waveforms of the modulated high voltage and count up/count down command signals are shown in fig. 1. Voltage jumps up to 8 kV with a rise time of 300 μs were used. In order to prevent loss of signal due to the slow response of the photo sensitive surface of the vidicon, a modulation frequency of only 0.5 Hz was employed.

Proper action of the whole Stark set-up was checked by measuring the Stark splitting of the first singlet state absorption of 2,4,5-trimethylbenzaldehyde in a durene host crystal. The measured Stark splittings were in good agreement with those calculated on basis of the detailed report on this system by Sheng et al. [10].

A computer program, carrying out the following procedures, was used to calculate the shift from the absorption and modulation spectra:

(1) Integrating twice the modulation spectrum (A) and once the absorption spectrum (B). The shift is directly given by the ratio A/B.

(2) Integrating the modulation spectrum and dividing by the calculated shift. The resulting spectrum should fit the absorption spectrum.

The latter procedure was used as a check.

3. Electrode effects

In previously described experiments [1] we used transparent tin oxide coated pyrex electrodes. However, with these electrodes in combination with unipolar high voltage modulation, the measured shifts were found to reproduce very badly. The observed shifts tended to decrease permanently in time, in some cases resulting in total disappearance under prolonged high voltage modulation. As careful filtering of the incident light decreased these effects, inhomogeneous fields varying in time caused by photochemically induced charge transport, probably together with charge injection from the electrodes, must be the reason. Such effects are well known now in linear Stark effect measurements [4], and should be even more bothersome in second order Stark effects. By changing from unipolar to bipolar electric field modulation the aging of the crystal was surpressed. The reproducibility of the results was further improved by using stainless steel instead of tin oxide coated electrodes.

Fig. 2 shows typical variations in measured shifts of the pentacene origins with applied electric field along the c'-axis of the host crystal, using tin oxide electrodes and the bipolar modulation method. Similar variations occur along the other crystal directions. For comparison also results obtained with stainless steel electrodes under the same experimental conditions, are given. In both cases a decrease of shift versus applied field is observed in time (aging), but in the tin oxide case this effect is dominated by much greater, less regular deviations. Therefore all measurements reported here were carried out with stainless steel electrodes, where the aging of the crystals was hardly noticeable during the experiment.

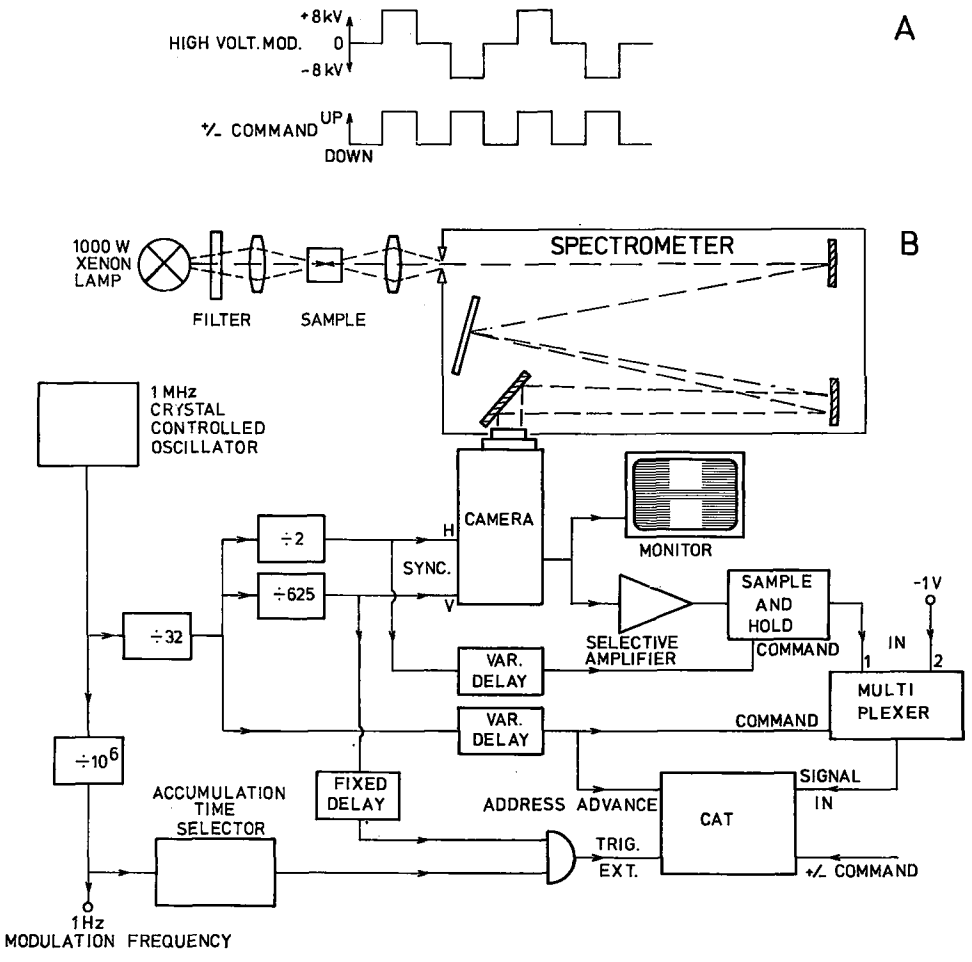

Fig. 1. (a) Wave forms used for obtaining the Stark modulation spectra. (b) Block diagram of the optical multichannel detection system.

4. Results

Both tetracene and pentacene show in their low temperature $^1B_{2u} \leftarrow {}^1A_g$ absorption spectrum in a *p*-terphenyl host crystal lines originating from different sites. In the case of tetracene only two sites are present with origins at 20 274 and 20 277 cm^{-1} [11]. The pentacene spectrum repeats from four different sites with origins located at 16 883, 16 887, 17 006 and 17 065 cm^{-1}. All tetracene and pentacene sites in *p*-terphenyl have the same polarization of the absorption and no difference in electric field induced shifts of these sites for either tetracene or pentacene was observed.

Fig. 3 shows some origin site spectra of tetracene and pentacene at 1.5 K obtained with the multichannel system. Accumulation times of about 5 minutes for the modulation, and 30 second for the absorption spectra were used. Fig. 3 further shows that the computer simulated curves, which are based on the assumption of only a second order Stark shift of the absorption lines, are in good agreement with the experimentally obtained Stark modulation spectra. This confirms our earlier suggestion [1] that the electric field induced intensity effect is negligible in these systems.

The electric field induced shifts of tetracene and pentacene, which all were found to be to the lower energy direction, are given, normalized at 1 kV/cm, in table 1.

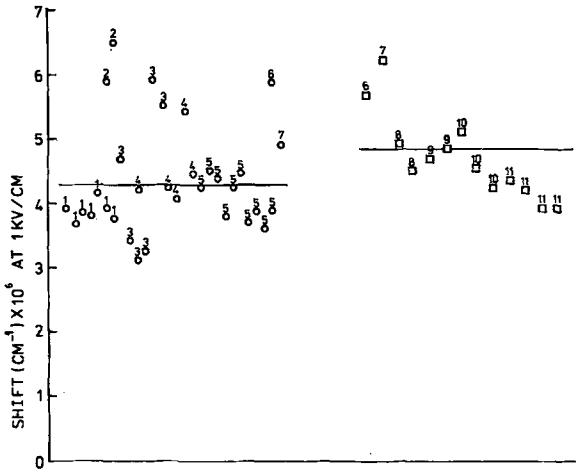

Fig. 2. Variation of the Stark shift of pentacene for a number of crystals using tin oxide (○) and stainless steel electrodes (□). The electric field was applied along the c'-axis of the p-terphenyl crystals. Numbers at the points, which are chronologically arranged, refer to the different crystals.

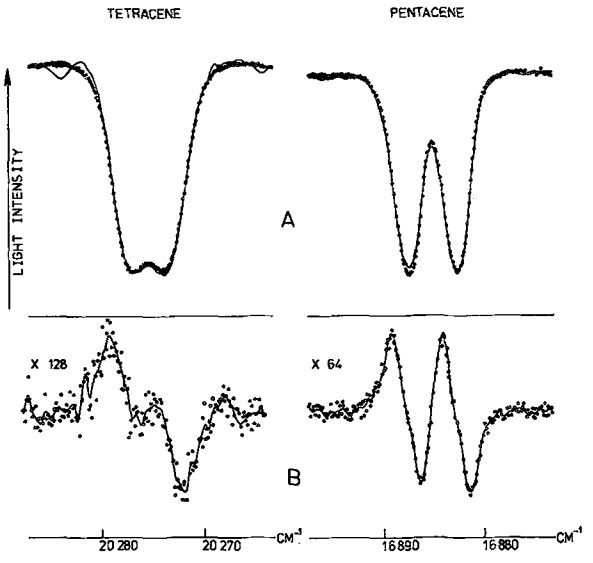

Fig. 3. Absorption (A) and Stark modulated spectrum (B), obtained with the optical multichannel detection system, of two sites of the electronic origin of tetracene and pentacene in p-terphenyl at 1.5 K. Points in the spectra are experimental values. The solid lines in the absorption spectra are calculated from the integrated modulation spectra while solid lines in the modulation spectra are obtained from a smoothing procedure and are further not used in the calculation. The electric field (45 kV/cm) was applied along the c'-axis of the crystal.

To study the influence of vibrational excitations on the polarizability, some Stark effect measurements were carried out on a totally symmetric vibronic level at 18 305 cm^{-1} (1 X 1423 cm^{-1}, [12]) in the pentacene absorption spectrum. We have found no significant different Stark shift of this line compared to the origin.

5. Side effects of the electric field modulation

Next to a difference in polarizability of molecular states, pressure effects exerted by the electrostatic attraction of the electrodes could also give rise to shifts with a quadratic electric field dependence.

Pressure effects on the spectrum of pentacene in a p-terphenyl host crystal were studied by Donnini [13], who reported a red shift of the absorption lines of about 15 cm^{-1}, when a pressure of 1 kilobar was uniformly applied over the crystal. We estimate the pressure exerted by the electrodes on the crystal in our experiments to be 1.3 X 10^{-6} bar at 1 kV/cm, assuming the space between the electrodes to be entirely occupied by the crystal ($\epsilon \approx 3$). The pressure induced shift should therefore be about 2 X 10^{-8} cm^{-1}. This is only a small fraction of the observed shifts and is further ignored for both tetracene and pentacene.

Table 1
Measured shifts (X $10^6 cm^{-1}$) scaled at 1 kV/cm, for the electronic origins of the $^1B_{2u} \leftarrow {}^1A_g$ transitions in tetracene and pentacene. Numbers between parentheses give respectively the numbers of measurements and crystals

Electric field direction	Tetracene		Pentacene	
a	0.81 ± 0.14	(6,2)	1.40 ± 0.24	(4,1)
b	1.39 ± 0.12	(7,2)	4.38 ± 0.17	(11,2)
c'	2.98 ± 0.1	(6,3)	5.33 ± 0.22	(13,5)

6. Discussion

6.1. Polarizability changes within the Lorentz approximation

In order to be able to convert the measured Stark shifts to molecular polarizability changes we have to know both the guest molecular orientation versus the

host crystal axes and the relation between the internal and external electric field.

Polarization measurements show that the short axes of both tetracene and pentacene are parallel to those of the *p*-terphenyl host molecules and there are strong steric arguments in favour of alignment of the guest and host long axes as well. We will therefore assume that the normal axes of these species are also parallel to one another. The direction cosines of the molecular versus the crystal axes of *p*-terphenyl were calculated from the data of Rietveld et al. [14] and are presented in table 2. The relation between the internal and external electric field, however, is less clear [5–7] but we will use here the anisotropic Lorentz approximation, realizing that the results obtained with this approximation must be handled with great cautiousness. Especially the neglect, in the Lorentz approximation, of the interaction between the induced dipoles in the guest with those of the host is probably not warranted in this case. As *p*-terphenyl is nearly orthorhombic ($\beta = 90°1'$) the principal directions of the ϵ-tensor are assumed to be parallel to the a, b and c'-axes of the crystal, which ensures that the internal electric field is parallel to the external one in these direction. Using the refractive indices reported by Sundararajan [15] we calculate for the anisotropic Lorentz factors:

$$L_a = 1.527, \qquad L_b = 1.615, \qquad L_{c'} = 1.946,$$

where L_i is defined as

$$L_i = F_{i,\mathrm{ext}}/F_{i,\mathrm{loc}} \qquad (i = a, b, c'),$$

where $F_{i,\mathrm{ext}}$ and $F_{i,\mathrm{loc}}$ respectively are the externally applied and local electric field along direction i. From the measured Stark shifts

$$\Delta\bar{\nu}_i = -\frac{1}{2hc} \sum_k \Delta\alpha_{kk} \cos^2\theta_{ik} F_{i,\mathrm{loc}}^2$$

($k = L,M,N$; θ_{ik} is the angle between direction i and k) along three orthogonal directions ($i = a, b, c'$), the difference polarizability tensor ($\Delta\alpha$) between the $^1B_{2u}$ excited and ^1A_g ground state of tetracene and pentacene can be determined. The principal values of the $\Delta\alpha$-tensor, calculated along these lines, for both tetracene and pentacene are found in table 3. The most surprising feature of table 3 is the fact that the $\Delta\alpha_{MM}$ values obtained, are so large, in fact for pentacene $\Delta\alpha_{MM}$ even exceeds $\Delta\alpha_{LL}$. This is against both our intuition and theoretical calculations [16]. From the fact that, within the same approximation, the $\Delta\alpha_{NN}$ values for both molecules are found to be negligible as expected, it is tempting to conclude that $\Delta\alpha_{MM}$ indeed is comparable to $\Delta\alpha_{LL}$ in these polyenes. However in view of the inherent approximations made in the calculation of the local field such a conclusion is not warranged as yet.

Table 2
Squared direction cosines for *p*-terphenyl

	L	*M*	*N*
a	0.086	0.266	0.648
b	5×10^{-5}	0.708	0.292
c'	0.921	0.027	0.061

6.2. Comparison with other data

Finally it is of some interest to compare our results with those previously obtained in solution or solid film, and this is done in table 4. The table also contains results of theoretical calculations, that show great variation in outcome.

We further note that the trace of the polarizability change obtained by us for tetracene is in good agreement with the value previously reported by Liptay et al. [2].

Concluding we may add that our principal values of $\Delta\alpha$ for tetracene should provide one with a better estimate than previously was possible [21] of the internal electric field in benzophenone.

7. Summary and conclusion

In this paper the full anisotropy of the second order

Table 3
Difference polarizability tensor components ($\times 10^{24}$ cm^3) for tetracene and pentacene between the $^1B_{2u}$ excited and ^1A_g ground state as calculated from the observed shifts and using the anisotropic Lorentz approximation

	Tetracene	Pentacene
$\Delta\alpha_{LL}$	29 ± 3	53 ± 4
$\Delta\alpha_{MM}$	25 ± 4	90 ± 8
$\Delta\alpha_{NN}$	5 ± 5	−11 ± 9

Table 4
Chronological survey of reported experimental and theoretical data ($\times 10^{24}$ cm^3) for $\overline{\Delta\alpha}$ ($=\frac{1}{3}|\Delta\alpha_{LL} + \Delta\alpha_{MM} + \Delta\alpha_{NN}|$) of tetracene and pentacene

	Tetracene		Pentacene	
	Theor.	Exp.	Theor.	Exp.
Trsic et al. [16]	$\overline{\Delta\alpha} = 19.8$		$\overline{\Delta\alpha} = 35.7$	
Liptay et al. [2]		$\overline{\Delta\alpha} = 25 \pm 4$, $\Delta\alpha_{MM} = 15 \pm 6$ a)		
Varma et al. [17]	$\overline{\Delta\alpha} = 56.6$	$\overline{\Delta\alpha} = 42.5$ b)		
Matzke et al. [18]	$\overline{\Delta\alpha} = 54.8$			
Barnett et al. [3]		$\frac{1}{2}\Delta\alpha_{MM} + \Delta\alpha_{LL} + \Delta\alpha_{NN} = 62 \pm 6$ c)		
Burrows et al. [19]	$\overline{\Delta\alpha} = 29.2$			
Blinov et al. [20]		$\overline{\Delta\alpha} \approx 15$ d)		
This work		$\overline{\Delta\alpha} = 20 \pm 4$ e)		$\overline{\Delta\alpha} = 44 \pm 7$ e)

a) Cyclohexane solutions, b) benzene solutions, c) in polystyrene film, d) thin solid film, e) p-terphenyl crystal.

Stark effect on the $^1B_{2u} \leftarrow {}^1A_g$ electronic transitions of tetracene and pentacene in a *p*-terphenyl mixed crystal at 1.5 K is reported.

It is shown that the observed Stark effects are only due to polarizability changes on excitation and that electric field induced intensity effects are negligible.

Within the anisotropic Lorentz approximation it is found that the long and short axis difference polarizability are comparable in these polyenes.

The quantitative treatment of the data, however, is still hampered by lack of knowledge of the internal electric field and calculations and experiments aimed at providing a better estimate of the internal field should have highest priority.

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References

[1] J.H. Meyling and D.A. Wiersma, Chem. Phys. Letters 20 (1973) 383.
[2] W. Liptay, G. Walz, W. Baumann, H.J. Schlosser, H. Deckers and N. Detzer, Z. Naturforsch. 26a (1971) 2020.
[3] G.P. Barnett, M.A. Kurzmack and M.M. Malley, Chem. Phys. Letters 23 (1973) 237.
[4] F.P. Chen, S.J. Sheng and D.M. Hanson, Chem. Phys. 5 (1974) 60.
[5] F.P. Chen, D.M. Hanson and D. Fox, J. Chem. Phys. 63 (1975) 3878, and references therein.
[6] D.A. Dunmur and R.W. Munn, Chem. Phys. 11 (1975) 297.
[7] F.P. Chen, D.M. Hanson and D. Fox, Chem. Phys. Letters 30 (1975) 337.
[8] L.W. Pickett, Proc. Roy. Soc. 142 (1933) 333.
[9] J.H. Meyling and W.H. Hesselink, submitted for publication.
[10] S.J. Sheng and D.M. Hanson, J. Chem. Phys. 60 (1974) 368.
[11] N.J. Kruse and G.J. Small, J. Chem. Phys. 56 (1972) 2985.
[12] A.F. Prikhotko, A.F. Skorobogatko and L.I. Tsikora, Optics and Spectrosc. 26 (1969) 115.
[13] J.M. Donnini, J. Chim. Phys. 71 (1974) 1543.
[14] H.M. Rietveld, E.N. Maslen and C.J.B. Clews, Acta Cryst. B 26 (1970) 693.
[15] K.S. Sundararajan, Z. Krist. 93 (1936) 238.
[16] M. Trsic, B.M. Uzhinov and P. Matzke, Mol. Phys. 18 (1970) 851; 24 (1972) 1431.
[17] C.A.G.O. Varma and L.J. Oosterhoff, Chem. Phys. Letters 8 (1971) 1.
[18] P. Matzke, O. Chacon, E. Sanhueza and M. Trsic, Intern. J. Quantum Chem. 6 (1972) 407.
[19] B.L. Burrows and A.T. Amos, Theor. Chim. Acta 36 (1974) 1
[20] L.M. Blinov and N.A. Kirichenko, Opt. Spectrosk. 37 (1974) 897.
[21] A.P. Marchetti and M. Scozzafava, Mol. Cryst. Liq. Cryst. 31 (1975) 115.